FEASIBILITY STUDIES ON A HYDROCARBON FUEL CELL

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INTRODUCTION

Work has been reported on several different types of hydrocarbon fuel cells, including those operating with molten carbonate electrolytes, and those with aqueous acid electrolytes at lower temperatures. Both of these cells suffer from serious corrosion problems, and also indicate that their operating efficiency may remain low because of (a) heat losses from the carbonate cell, and (b) high polarization of the anode in the acid cell.

Since one of the major claims of the fuel cell is its high efficiency, it is well to examine carefully the overall efficiency of any hydrocarbon fuel cell, considering both the operating cell voltage and the utilization efficiency of the fuel.

One of the most efficient fuel cells is the modified "Bacon" cell, a H_2/O_2 cell operating with nickel electrodes at 4-500°F in concentrated alkaline electrolyte. This cell has exhibited current densities of over 300 asf at 1.0 volt at which voltage most other cells are barely producing any current at all. However, the alkaline electrolyte precludes the direct use of a carbon-containing fuel.

Previous work has been reported (1) on the use of palladium membrane anodes in 400°F KOH-electrolyte fuel cells. Such an anode, permeable to hydrogen only, permits the use of impure hydrogen, containing CO_2 and CO, and high currents and efficiencies have been demonstrated. More recently (2) a cell has been described in which methanol and steam are reacted on a catalyst in contact with a palladium membrane anode. At 400°F, this reaction proceeds rapidly, almost to completion.

One can also consider the use of a hydrocarbon in a cell of similar configuration (3). Hydrocarbon-steam reactions take place on cheap nickel catalysts, and the use of thin palladium-silver alloy film anodes, paired with a nickel cathode, presents the concept of a relatively cheap and highly efficient hydrocarbon fuel cell, in which the reforming catalyst does not have to be compatible with the electrolyte.

The Internal Reforming Anode Concept

Figure 1 represents a schematic of the "internal reforming anode cell."
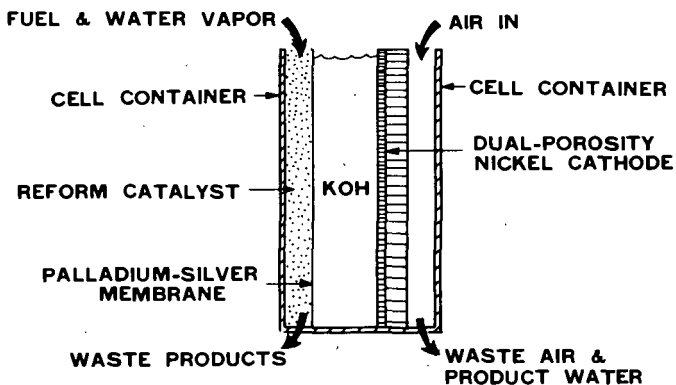

Figure 1. Schematic Diagram of Hydrocarbon-Air Fuel Cell

Hydrocarbon/steam mixture is fed into the gas-space of the cell which is packed with catalyst. Hydrogen, CO and CO_2 are produced. The hydrogen permeates through the palladium anode and enters into a conventional fuel cell reaction. The other electrode is a biporous oxidized nickel structure fed with CO_2-free air.

Hydrocarbon-steam reforming reactions are normally carried out at temperatures around 1500°F. The Bacon fuel cell, however, is limited to a maximum temperature of about 500°F, by the maximum service temperature of the Teflon insulating gaskets, and by the onset of unacceptable corrosion rates at the cathode. At 500°F the equilibrium hydrogen production from a hydrocarbon will be very low, and one might predict very poor fuel utilization. As current is drawn from the cell, however, hydrogen is extracted from the equilibrium mixture, forcing the reaction to proceed. In this way, it is theoretically possible to obtain 100% conversion of the fuel, even at 500°F. The rate of the reaction, however, at such a low temperature is completely unknown, and can only be found by experiment.

Experiments were set up, therefore, to test the feasibility of this cell concept, operating on a number of different hydrocarbon fuels. Primarily, it was required to know if the hydrogen production reaction could proceed fast enough at these temperatures to sustain useful currents, and if hydrogen could be extracted through the palladium anode at a high enough rate to obtain high fuel utilization.

Apparatus

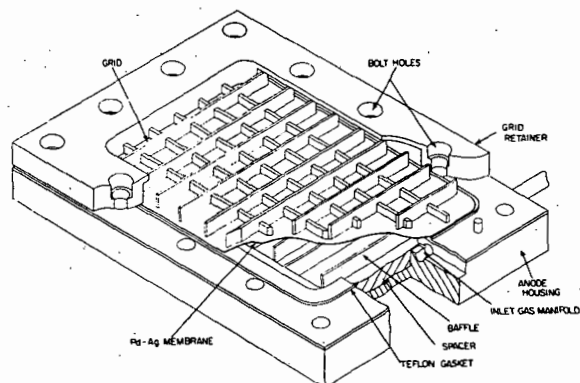A rectangular anode holder was constructed as shown in Figure 2.

Figure 2.   Cutaway of Anode Assembly

The palladium-silver alloy foil was clamped across the face of a shallow recessed plate, to form a closed cavity.   This cavity was packed with a commerical supported-nickel reforming catalyst.   Gas was fed in and taken out by two galleries along opposite edges of the cavity.   The palladium foil was prevented from bowing inwards by the catalyst and outwards by a nickel criss-cross grid.

This anode holder was immersed in a tank of 85% KOH maintained at 500°F, and a dual-porosity nickel cathode welded into a dished plate to form a gas cavity, was suspended close to the anode from a lid which sealed the KOH from the air.   Figures 3 and 4 show this arrangement clearly.   A 1/8" diameter palladium-silver tube, fed with hydrogen, was suspended from the lid to serve as a reference electrode.
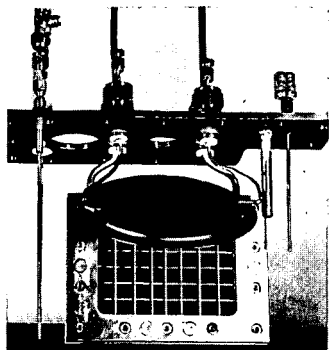
Figure 3.   Hydrocarbon Fuel Cell
            Assembly with Cathode
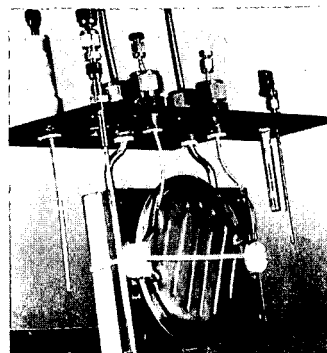   Bent Back

Figure 4.   Hydrocarbon Fuel Cell
            Assembly

The anode was supplied with an accurately metered mixture of hydrocarbon and steam, preheated to 500°F. The exit gas was cooled, passed through a palladium-tube hydrogen detector, and analyzed by means of a chromatograph. Flow rates were recorded by a bubble meter at the exit, and the system pressure was controlled by a manostat in the vent line. A schematic of the system is shown in Figure 5.
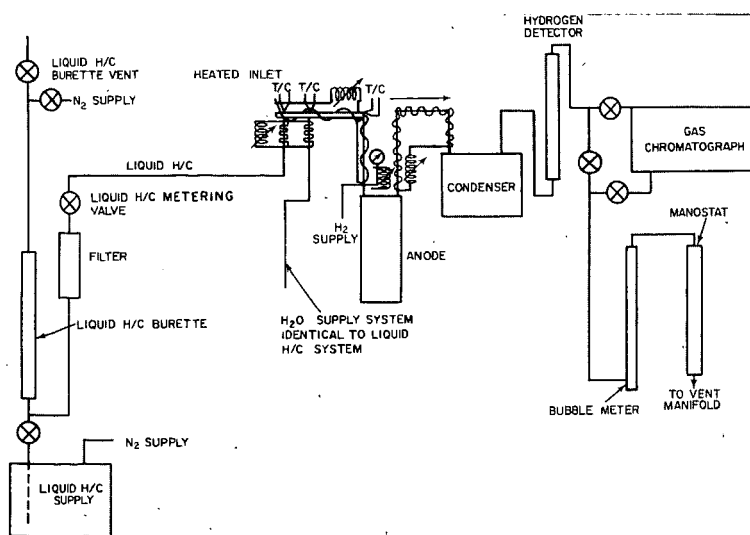

Figure 5.   Schematic of Hydrocarbon Anode System

RESULTS

The cell was operated on n-octane, methane and a commercial kerosene fuel, JP-150, with very encouraging results. Figure 6 shows half-cell and full-cell polarization curves for octane-air. The electrode spacing was 0.59 inch. It will be seen that 80 amps/ft^2 was obtained at a cell terminal voltage of 0.75V, with a fuel flow corresponding to a utilization of 45%.
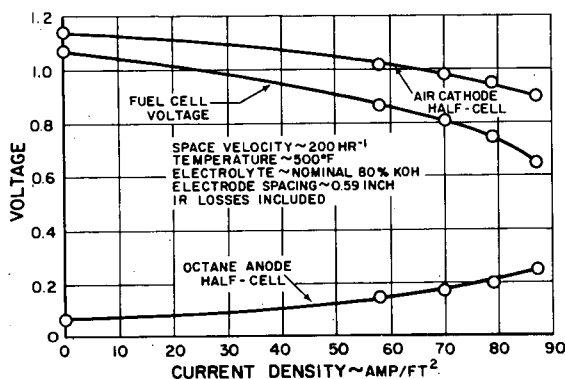
Figure 6. Experimental Performance of Air-Octane Fuel Cell

Under similar conditions, methane also gave 80 amps/ft^2 at 0.75 V and 45% fuel utilization, and JP-150 gave 68 amps/ft^2 at 0.75 V at 35% utilization (Figure 7).
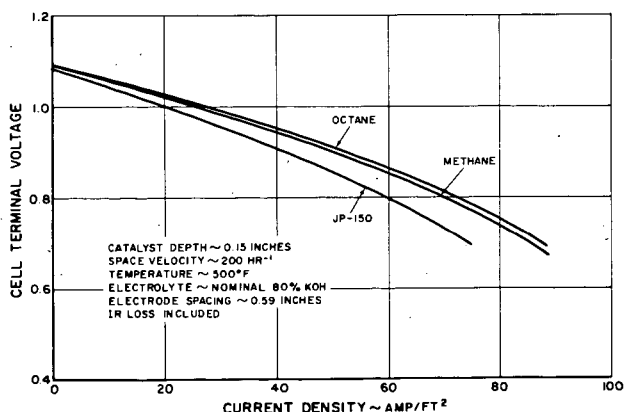
Figure 7. Comparison of Various Fuels in the Internal Reforming Cell

In order to increase the fuel utilization, it is necessary to reduce the fuel flow rate. To study the effect of fuel flow rate on current density, the anode was maintained at a constant polarization, (0. 15 V from an unpolarized hydrogen electrode). There is a direct relationship between the fuel flow rate, current density, and fuel utilization. As fuel flow is increased, unless a higher current flows, the utilization simply falls off. Figure 8 shows fuel flow (ideal hydrogen space velocity) plotted against current density. The sloping lines are lines of constant utilization.
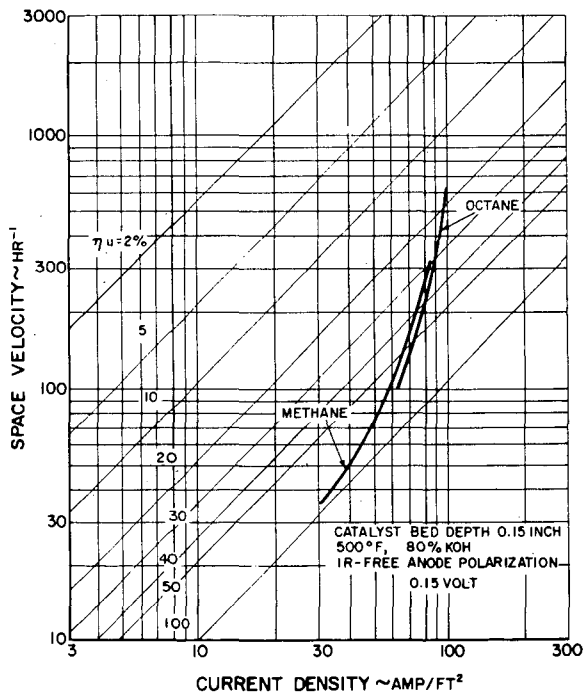

Figure 8. Relationship Between Fuel Flow Rate, Current and Fuel Utilization for Constant Anode Polarization of 0. 15 Volts

The curves on Figure 8 indicate the variation of current with varying fuel flow at a fixed polarization for octane and methane. The curves would be displaced slightly to the left for lower polarizations and vice-versa. It was possible to run the cell on methane with a 70% fuel utilization; but in order to achieve the highest utilizations, the penalty in current density became severe. In other words, the current is limited by the fuel supply when higher utilizations are attempted. This suggests that the catalytic production of hydrogen is too slow to sustain high currents and utilizations.

If the rate of the catalytic reforming reaction is limiting, an improvement in performance might be expected by using a thicker catalyst bed. Figure 8 was obtained with a catalyst bed thickness of 0.15 inches. The anode was made in such a way that bed thicknesses of 0.30" and 0.60" could be obtained. Increasing the bed thickness to 0.60" did indeed give higher current densities, up to 175 amps/ft^2, at the same space velocity and polarization. However, in order to obtain the same space velocity with a larger bed volume, higher actual fuel flow rates were required, and this had the effect of reducing the fuel utilization to about 30%.

It became clear at this point that considerable optimization of anode design would have to be done in order to trade-off between the currents, cell volumes and efficiencies associated with varying the catalyst bed thickness.

Since the effect of the quantity of the catalyst is so marked, a study was made of the reforming reaction itself, in order to see how its kinetics were affected by the extraction of hydrogen. This study was carried out by analysis of the exit gases vented from the anode.

Using n-octane as fuel, we consider the following possible reactions:

1. Fuel conversion to CO and H_2.

2. Shift of CO to CO_2 (assumed complete at this temperature).

3.   Conversion of CO and H_2 to form methane.

4.   Extraction of hydrogen by the anode process. (Figure 9)

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                                    METHANE
                                       +
                                     STEAM
                           (3)
   HYDROCARBON        CO
        +        (1)   +
     STEAM            H₂
                           (2)
                               CO₂    (4)      ANODIC
                                +         →   OXIDATION
                               H₂             OF  H₂
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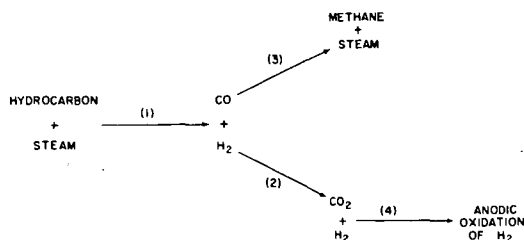
Figure 9. Schematic of Reaction Paths

    The third reaction is an undesirable one, since it removes hydrogen from the equilibrium mixture. It is catalyzed by the same catalysts that promote the desirable reaction (1).

    First, we studied the amount of unconverted fuel appearing in the exhaust. This gives a measure of the rate of reaction 1. We were surprised to find that although no unreacted fuel is found at first, it begins to show up after about 5 hours, progressively increasing, indicating that the catalyst decays quite rapidly. Figure 10 shows the decrease of the fuel conversion with time. Notice that the decay is not so apparent when the cell is on load - when the fuel utilization of the cell reaches 50%, a much higher proportion of the fuel fed in is converted. This would be expected since the effect of extraction of hydrogen is to increase the rate of the hydrogen-forming reaction.
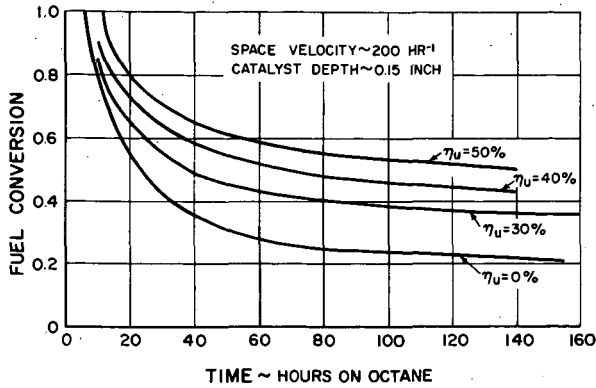
Figure 10. Comparison of Catalyst Aging Effect on Octane Fuel Conversion
at Utilization Efficiencies of 0, 30, 40 and 50 Percent

Secondly, we observed the amount of methane appearing in the cell exhaust. This

gives an indication of the rate of reaction 3. Figure 11 shows the "Reform Conversion"

as it changes with time. The "Reform Conversion" is the proportion of the converted

fuel which produces hydrogen, rather than methane. In the ideal case it is 1.0. It will

be seen that at no-load conditions, the reform conversion remains low, indicating most
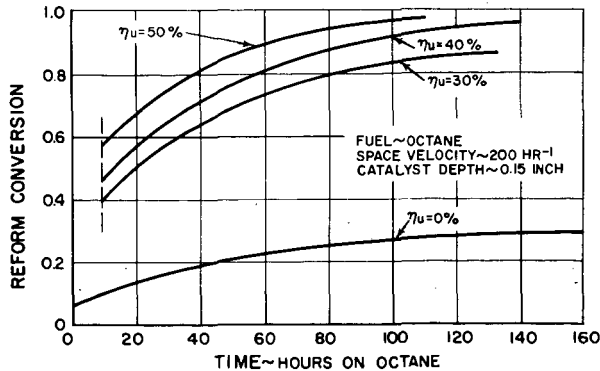
of the fuel is being converted to methane.

Figure 11. Comparison of Catalyst Aging Effect on Reform Conversion
at Utilization Efficiencies of 0, 30, 40 and 50 Percent

When hydrogen is extracted from the equilibrium, all processes producing hydrogen tend to be favored. This includes the reverse of the methane-producing side reaction, so methane formation is suppressed. This is shown on Figure 11, where the initial "Reform Conversion" is as high as 0.55 when the fuel utilization is 50%. The Reform Conversion increases with time as the catalyst decays. Since less hydrogen is produced, so a higher proportion of it gets extracted by the anode, and the tendency for methane formation becomes less.

The most important conclusion here is that the catalytic reaction changes radically with hydrogen extraction, so that little useful information will be learned from studying the reaction in a conventional reactor.

Thirdly, attention was paid to the hydrogen content of the exhaust stream. This gives an indication of the rate of reaction 4. Figure 12 shows that over 90% of the hydrogen produced in the catalyst bed is extracted as "current" through the anode, and the amount increases slightly with time.
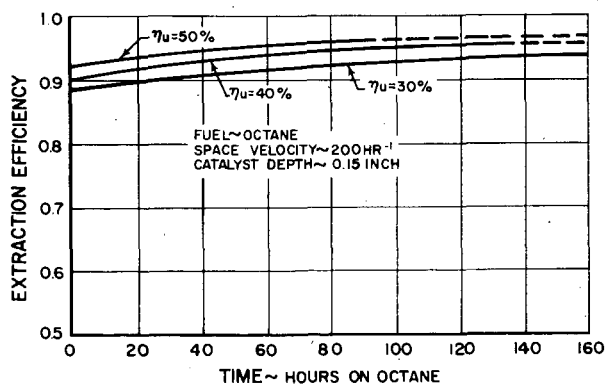

Figure 12. Comparison of Catalyst Aging Effect on Extraction Efficiency at Utilization Efficiencies of 30, 40 and 50 Percent

The sum total of these time effects on the performance of the cell is not very marked. As the catalyst decays, more unreacted fuel is vented. Of the hydrogen formed, less is reconverted to methane, and the total hydrogen production remains almost constant. The net result of this is that the cell performance, as measured by current density at a given polarization, only falls slowly for 50 hours or so, then begins to decrease as the catalyst decay becomes really severe. This is illustrated in Figure 13. This accounts for the fact that the cell appears to be stable for short term operation, though examination of the vent gases would show a dramatic change during the first 24 hours of operation.
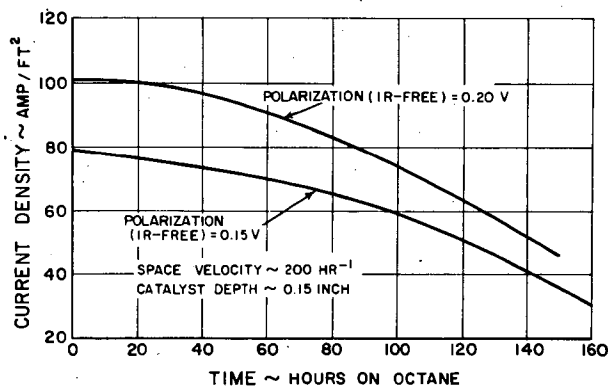

Figure 13. Comparison of Catalyst Aging Effect on Current Density with Octane Fuel at APV = 0.20

In the case of methane fuel, a much reduced decay rate was observed. A cell was run for a total of 730 hours at a constant anode potential of .015V. The current density changed only from 65 amps/ft^2 to 50 amps/ft^2 and the fuel utilization from 80% to 60%. The methane system exhibits another clear difference over liquid hydrocarbons: There is no complication of the methane-producing side reaction, and the equilibrium partial pressure of hydrogen for any degree of extraction may be calculated thermo- dynamically. By comparing the performance of an internal reforming anode with that

of a palladium anode fed with hydrogen at the calculated equilibrium partial pressure,
it should be possible to examine the rates of the reform reaction and the extraction
process separately. This work is at present in progress.

CONCLUSION

This work has shown that the demonstrated performance of the internal reforming
hydrocarbon cell, in terms of current-voltage curves and utilization efficiency, is
superior to that of other direct hydrocarbon systems.

However, a closer look at the system indicates that one can easily be misled
by a single consideration of current-voltage curves for hydrocarbon fuel cells. Considera-
tion of the fuel utilization efficiency requirement dictates that the higher current densities
demonstrated may be unfeasible from an efficiency standpoint. There will be a difficult
optimization process between cell volumes, catalyst bed thickness, maximum current
density and cell efficiency. This optimization will vary for different catalysts, operating
temperature and cell design, so cannot be attempted at this stage.

With present technology the current density obtainable at overall cell efficiencies
of greater than 60% are still below 100 a/ft^2 and have to be increased before a com-
mercially attractive cell can be built. Present indications are that the catalytic reforming
of the fuel at 500°F is limiting the reaction, so that improved catalysts will be needed.
The catalyst used in this work not only had too low an activity at 500°F, but also decayed
rapidly with time at this temperature. Up to now there has never been an incentive to
develop catalysts for this reaction for a thermodynamically unfavorable temperature
region.

All of the work reported here was done with 1.5 mil thick foil anodes. A reduction
of thickness by a factor of 3 to 5 may be needed to obtain economic feasibility. Such
a reduction in thickness will also bring about higher current densities due to higher

hydrogen transport, so another optimization of material cost, power density and technical fabrication will be required.

During the operation of the internal reforming cell, we have learned that time-decay effects can be far from obvious, and only a careful monitoring of all the separate processes going on in a complex system can show whether a decay effect is occurring. Otherwise a decay may be compensated by another variable for long periods of time, only to appear as a performance loss at a later point.

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